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PATENT APPLICATION

Docket No.:D502

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Title:

Conducting Polymer Nanofiber Sensors

SPECIFICATION

Statement of Government Interest

The invention was made with Government support under
contract No. F04701-00-C-0009 by the Department of the Air
Force. The Government has certain rights in the invention.

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Reference to Related Application

The present application is related to applicant's
copending application entitled "Synthetic Method for Conducting
Polymer Nanofibers", S/N: xx/xxx,xxx, filed yy/yy/yy, by the
same inventors.

Field of the Invention

The invention relates to the field of nanostructured polymers. More particularly, the present invention is related to methods of manufacture of conducting polymer nanofibers and sensors made of conducting polymer nanofibers.

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Background of the Invention

Since the discovery that conjugated polymers can be made to conduct electricity through doping, research has been extended in the field of conducting polymer films. Polymers have been made as conducting links of organic monomers having defined chemical structures. Polyaniline can be made as a conducting polymer of aniline monomers. Polyaniline is a unique conjugated polymer in that polyaniline can be tailored for specific applications through a non-redox acid and base doping process. Polyaniline has been studied for electronic and optical applications, such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors. Unlike other conjugated polymers, polyaniline has a simple and reversible acid doping and base dedoping chemistry enabling control over properties of the polyaniline, such as density, solubility, conductivity, and optical absorption. One-dimensional polyaniline nanostructures, including nanowires, nanorods, and nanotubes possess low-dimensional sizes and organic conduction. The electrically conductive form of polyaniline is known as emeraldine having an oxidation state which, when doped with an acid, protonates the imine nitrogens on the polymer backbone and induces charge carriers. The conductivity of polyaniline increases with doping from the undoped insulating emeraldine base form, $\sigma < 10^{-10}$ S/cm, to the fully doped, conducting emeraldin salt form, $\sigma > 1$ S/cm. Dopants can be added in any desired quantity until all imine nitrogens, that is half of the total nitrogens, are doped, by

1 controlling the pH of the dopant acid solution. Dopants can be
2 removed by interacting the emeraldine salt form with common
3 bases such as ammonium hydroxide.

4
5 Conducting polymers can be used in sensors having optical,
6 electrochemical and conducting properties. Conducting polymers
7 are unique by changing properties when chemically treated with
8 oxidizing or reducing agents. After chemical treatment with
9 protonating, deprotonating, oxidizing or reducing agents, the
10 conducting polymer polyaniline can reversibly change from an
11 initially electrically insulating state to a conducting state.
12 This transition can be used in such applications as optical
13 sensors, chemical sensors, and biosensors. Conducting polymers
14 include polyaniline, polypyrrole, polythiophene, and their
15 derivatives. Polyaniline is a conducting polymer that is
16 environmentally stable and can react with chemical species at
17 room temperature. As such, polyaniline may be suitable for gas
18 sensing applications using processes that create a uniform thin
19 film of the polyaniline. This thin film may then react with
20 protonating and deprotonating agents to create a conduction
21 pathway that can easily be measured.

22
23 The conductivity depends on both the ability to transport
24 charge carriers along the polymer backbone and the ability of
25 the carriers to hop between polymer chains through interpolymer
26 conduction. Any interactions with polyaniline that will alter
27 either of these conduction processes will affect the overall
28 conductivity. This is the underlying chemical property enabling

1 polyaniline to be used as the selective layer in a chemical
2 vapor sensor, such as, a resistance detector generally known as
3 a chemiresistor. Due to room temperature sensitivity, the use
4 of deposition onto a wide variety of sensor substrates and due
5 to the various structures, conducting polymers are potential
6 materials for sensor applications. A polymer chemiresistor
7 would typically consist of a substrate, electrodes, and a
8 conducting polymer selective thin film. Changes in conductivity
9 of the polymer film upon exposure to chemical vapors can be
10 readily monitored with an ohmmeter or electrometer. Polyaniline
11 sensor research has focused on changing the polymer structure
12 to facilitate interaction between vapor molecules and the
13 polymer either by modifying the polymer backbone or the
14 interchain connections. However, poor diffusion can readily
15 outweigh any improvements made to the polymer chains because
16 most of the material other than the limited number of surface
17 sites, is not available for interacting with a chemical vapor,
18 thus degrading sensitivity. One way to enhance diffusion is to
19 reduce film thickness, such as producing monolayers of
20 conventional polymer materials, which leads to a trade-off
21 between sensitivity and robustness. Coating polyaniline on
22 porous substrates can increase the surface area, but the
23 chemistry and physics involving polymer support and polymer
24 electrode interfaces is not well defined for practical use.

25
26 Nanostructured polyaniline, such as nanowires, nanofibers,
27 nanotubes, and nanorods may have sufficiently high surface area
28 and faster diffusion rates of gas molecules into the

1 nanostructures for use as chemical sensors with increased
2 sensitivity, as compared to bulk polyaniline. For xample, the
3 surface area per unit mass S_A of polyaniline nanofibers
4 increases geometrically as the diameters d of the nanofibers
5 decrease, that is $S_A \sim 1/d$. Even when the thickness of an ultra-
6 thin film is the same as the diameters of the nanofibers, the
7 fibers may outperform a thin film because the fibers have
8 higher surface-to-volume ratios due to their cylindrical
9 morphology. The small diameter of the nanofibers, for example
10 less than 500 nm, coupled with the possibility of gas
11 approaching from all sides should give sensors with improved
12 performance. Despite the high surface area and porosity
13 associated with nanostructures, nanostructured polyaniline has
14 not been used as chemical sensors. This is due to uncertain
15 nanostructure characterization as well as the lack of reliable
16 methods to make high quality polyaniline nanofibers, and
17 reliable methods to coat surfaces with polyaniline nanofibers.
18 No practical nanostructured conducting polymer sensors are
19 available due to the lack of reliable methods for making high
20 quality conducting polymer nanostructures in bulk quantities
21 and the unknown properties of nanofiber characterization.

22
23 Syntheses of polyaniline nanostructures have been carried
24 out both chemically and electrochemically by polymerizing the
25 aniline monomers with the aid of either a hard template or a
26 soft template. Examples of hard templates include zeolite
27 channels, track-etched polycarbonate, nanoporous membranes, and
28 anodized alumina. Examples of soft templates for self-assembly

1 of functional polymers include surfactants, poly lectrolytes,
2 or complex organic dopants, such as micelles, liquid crystals,
3 thiolated cyclodextrins, and polyacids, that may be capable of
4 directing the growth of polyaniline one-dimensional
5 nanostructures with diameters smaller than 500 nm. Adding
6 structural directing molecules such as surfactants or
7 polyelectrolytes to the chemical polymerization bath is one way
8 to obtain polyaniline nanostructures. When organic dopants with
9 surfactant functionalities are used, emulsions or micelles can
10 be formed leading to microtube, microfiber, or microrod
11 structures. However, when polyaniline nanostructures with
12 diameters of less than 500 nm are desired, then very complex
13 dopants with bulky side groups are needed, such as sulfonated
14 naphthalene derivatives, fullerenes, or dendrimers.

15
16 The formation of polyaniline nanostructures
17 disadvantageously relies either on guidance from hard templates
18 or self-assembled soft templates. These templates
19 disadvantageously use complex synthetic conditions that require
20 the removal of such templates and hence provide low yields and
21 with poor reproducibility. Chemical methods of making
22 polyaniline nanostructures, such as nanotubes, nanofibers,
23 nanowires, and nanorods, disadvantageously require specific
24 structure-directing template materials added into or applied to
25 the polymerization bath. The synthetic conditions
26 disadvantageously have to be carefully designed to accommodate
27 formation and purification to obtain pur polyaniline
28 nanostructures. These template methods are disadvantageously

1 dependent on either a template or a specific complex chemical
2 reagent, and post-synthetic treatments are needed to remove the
3 reagent from the byproducts in order to recover pure
4 nanostructured polyaniline. Therefore, developing synthetic
5 production methods that do not rely on templates, structural
6 directing molecules, or specific dopants is desirable,
7 especially for scaling up to produce large quantities of
8 nanostructured materials suitable for mass usage in chemical
9 sensors.

10
11 Electrochemical polymerization and physical methods, such
12 as electrospinning and mechanical stretching can produce
13 conducting polymer nanofibers without templates, but these
14 conducting polymer nanofiber materials can only be made on
15 carefully prepared surfaces offering limited production
16 scaling. Electrochemical synthesis of polyaniline has indicated
17 that some nanofibers form naturally on a synthesis surface
18 while the underlayer is much more compact with microfiber
19 polymers. For the production of polyaniline nanofiber sensors
20 in quantity, there exists a need for a practical bulk synthetic
21 method. Despite the variety of current synthetic methods
22 available to produce polyaniline nanostructures, there is a
23 need for a practical synthetic method capable of making pure,
24 uniform, and template-free polyaniline nanostructures with
25 predetermined small diameters and in bulk quantities. Current
26 synthetic methods are not useful in mass production of ultra-
27 small, low-dimensional structures, such as sensors, using
28 conductive polymer nanofibers of polyaniline. These and other

1 disadvantages are solved or reduced using the present
2 invention.

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Summary of the Invention

An object of the invention is to provide a method for forming a conductive polymer.

Another object of the invention is to provide a method for forming conductive polymer nanofibers.

Another object of the invention is to provide a method for forming conductive polymer nanofibers with predetermined diameters.

Yet another object of the invention is to provide a method for forming conductive polymer polyaniline nanofibers.

A further object of the invention is to provide a method for forming and purifying conductive polymer polyaniline nanofibers in a polymerization bath suitable for production scaling in bulk quantities.

Still another object of the invention is to provide chemical sensors made from conductive polymer polyaniline nanofibers.

Yet a further object of the invention is to provide chemical sensors made from conductive polymer polyaniline nanofibers having strong adherence to conducting terminals.

1 The invention is directed towards methods for producing
2 conducting polymer nanofibers and chemical sensors made of
3 conducting polymer nanofibers. In a preferred form, conducting
4 polyaniline nanofibers are produced in a polymerization bath,
5 suitable for batch bulk production and suitable for making a
6 variety of chemical sensors. Polyaniline nanofibers can be
7 doped with an acid and dedoped using a base, in a reversible
8 chemical process. Discovery is made that nanostructured
9 polyaniline has greater sensitivity and faster chemical time
10 responses than the bulk form due to higher effective surface
11 areas and shorter penetration diffusion depths for gas
12 molecules. Discovery is further made that a thiol film on the
13 gold terminals adheres to polyaniline nanofibers for securing a
14 nanofiber polyaniline thin film to a gold conductor. Discovery
15 is further made that polyaniline nanofibers, having diameters
16 less than 500 nm and lengths less than 10 μm , in a thin film
17 have sufficient conductivity changes in response to dopants and
18 dedopants to be suitable for use in chemical sensors. Discovery
19 is also made that selective acids used during polymerization of
20 the polyaniline nanofibers predetermine the resulting diameter
21 of the nanofibers. In the preferred form, an acid and base
22 chemical vapor sensor can be made using conventional gold
23 sensor terminals covered by a polyaniline nanofiber thin film.

24
25 In the preferred form, polyaniline nanofibers can be
26 uniformly produced with predetermined diameter sized nanofibers
27 having predetermined lengths in a normal distribution. During
28 polymerization, a selected acid is used to efficiently

1 facilitate the polymerization process, which is selected to
2 predetermine a normal distribution of diameters of the product
3 polymer nanofibers. Each different diameter nanofiber has a
4 resulting different chemical response, and hence, the
5 polymerization process can be tailored to specific performances
6 of the chemical sensors. These polyaniline nanofibers can then
7 be used in a variety of chemical sensors, such as acids, bases,
8 alcohols, volatile organic chemicals and reducing agents. The
9 resulting thin film sensors made of the nanofibers have
10 superior performance in both sensitivity and time response to a
11 variety of gas vapors. Exemplar acids include hydrochloric
12 acid, sulfuric acid, nitric acid, perchloric acid, and
13 camphorsulfonic acid. Exemplar bases include ammonia and
14 butylamine. Exemplar alcohols include methanol, ethanol, and
15 propanol. Exemplar volatile organic chemicals include
16 chloroform and nitromethane. Exemplar reducing agents include
17 hydrazine.

18
19 In the general form, polymer nanofibers can change
20 physical properties such as conductivity, density,
21 conformation, oxidation state, and optical absorption, among
22 others, offering a wide variety of sensors for sensing various
23 materials. Polyaniline nanofibers with uniform diameters have
24 predetermined response characteristics. The polyaniline
25 nanofibers can be made in bulk quantities through a facile
26 aqueous and organic interfacial polymerization method at
27 ambient conditions. The nanofibers have varying lengths within
28 a normal distribution and form interconnected networks as a

1 thin film of polyaniline. In the general form, the invention is
2 directed to a synthesis method for producing polymer nanofibers
3 well suited for use in chemical sensors. In the preferred form,
4 the method is suitable for bulk production of polyaniline
5 nanofibers for use in acid and base chemical sensors. The
6 synthesis method is preferably applied to organic monomers that
7 can be linked into conducting polymers, such as polyaniline,
8 polypyrrole, polythiophene and their derivatives. A template-
9 free process using an aqueous polymerization bath provides a
10 practical bulk synthetic method capable of producing bulk
11 quantities of pure and uniform nanofibers with small
12 predetermined diameters. The synthesis method is based on
13 chemical oxidative polymerization of the monomers. The
14 polymerization process is perfected in an immiscible, organic-
15 aqueous, two-phase system. The synthetic method yields polymer
16 nanofibers with nearly uniform reproducible diameters. These
17 and other advantages will become more apparent from the
18 following detailed description of the preferred embodiment.

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Brief Description of the Drawings

Figure 1A is a chemical diagram of doped polyaniline emeraldine salt.

Figure 1B is a chemical diagram of undoped polyaniline emeraldine base.

Figure 2 is a process flow of a method for synthesizing polyaniline nanofibers.

Figure 3 is a process flow of a method for forming an acid sensor.

Figure 4A is a graph of polyaniline nanofiber time response to an acid dopant.

Figure 4B is a graph of polyaniline nanofiber time response to a base dedopant.

Figure 5 is a process flow of a method for forming a polyaniline nanofiber precoated sensor.

Figure 6 is a block diagram of a polyaniline nanofiber precoated sensor.

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Detailed Description of the Preferred Embodiment

An embodiment of the invention is described with reference to the figures using reference designations as shown in the figures. Referring to Figures 1A and 1B, monomers, such as aniline monomers can be linked together to form polyaniline. The polyaniline can be doped with an acid, such as hydrochloric acid HCl dopant, as shown in Figure 1A, and can be dedoped with a base, such as, ammonia NH_3 .

Referring to Figures 1A, 1B, and 2, and more particularly to Figure 2, a seven-step method of synthesizing polyaniline nanofibers relies on a facile chemical process to produce high quality polyaniline nanofibers under ambient conditions using an aqueous-organic interfacial polymerization.

In step 1, a catalysis solution is first formed from water, an acid, and an oxidizer. The acid is preferably hydrochloric acid HCl, but other acids may be used, such as sulfuric acid H_2SO_4 , nitric acid HNO_3 , perchloric acid HClO_4 , phosphoric acid H_3PO_4 , acetic acid CH_3COOH , formic acid HCOOH , tartaric acid $\text{C}_4\text{H}_6\text{O}_6$, methanesulfonic acid $\text{CH}_3\text{SO}_3\text{H}$, ethylsulfonic acid $\text{C}_2\text{H}_5\text{SO}_3\text{H}$, 4-toluenesulfonic acid $\text{C}_7\text{H}_7\text{SO}_3\text{H}$, and camphorsulfonic acid (CSA). The oxidizer is preferably ammonium peroxydisulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$, but other oxidizers may be used, such as iron chloride FeCl_3 and other peroxydisulfate derivatives such as $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$. In step 2, a monomer solution is formed from a solution of a nonconducting monomer and an organic solvent.

1 In the preferred form, the monomer is aniline, but other
2 carbon-based organic monomers can be used, such as pyrrol ,
3 thiophene, toluidine, anisidine and other derivatives of
4 aniline such as methylaniline, ethylaniline, 2-alkoxyaniline,
5 and 2,5 dialkoxyaniline monomers, for forming polyaniline,
6 polypyrrole, polythiophene, polytoluidine, polyanisidine,
7 polymethylaniline, polyethylaniline, poly2-alkoxyanilines and
8 poly2,5-dialkoxyanilines respectively. The organic solvent is
9 preferably carbon tetrachloride (CCl_4), but other organic
10 solvents may be used, such as benzene, toluene, chloroform,
11 methylene chloride, xylene, hexane, diethylether,
12 dichloromethane and carbon disulfide. In the preferred form,
13 aniline monomers are dissolved in carbon tetrachloride (CCl_4).
14

15 In step 3, the monomer solution is disposed in a reaction
16 vessel that can be scaled from small to large for increased
17 batch production of bulk polymer nanofibers. In step 4, the
18 catalysis solution is disposed nonturbulently into the reaction
19 vessel and onto the monomer solution forming a bifurcated
20 mixture having an aqueous organic reaction interface between
21 the lower monomer solution and the upper floating catalysis
22 solution. In step 5, a polymerization reaction occurs at the
23 aqueous organic reaction interface creating conductive doped
24 nanofiber polyaniline forming in the upper aqueous catalysis
25 solution. The catalysis solution becomes a polymer solution
26 comprising polymers of linked monomers from the monomer
27 solution. As the catalysis solution becomes a polymer solution,
28 the monomer solution is depleted of monomers and becomes an

1 organic solution. Aniline polymerizes at the interface between
2 the bottom organic monomer solution containing dissolved
3 aniline and the upper aqueous catalysis solution containing the
4 oxidant and dopant. As the polymerization reaction proceeds,
5 polyaniline nanofibers form across the interface, slowly
6 diffusing and dispersing into the upper aqueous catalysis
7 solution and eventually filling the upper aqueous solution with
8 dissolved polyaniline nanofibers. At the same time, the color
9 of the lower organic layer turns red-orange due to the
10 formation of by-products, such as aniline oligomers. The
11 nanofiber product in the upper organic solution is then
12 collected and purified by conventional processes such as either
13 dialysis or filtration, yielding a nanofiber product in the
14 form of a water dispersion or a powder, respectively. Further
15 washing or dialyzing with water yields pure, doped polyaniline,
16 which can be dedoped by washing or dialyzing with a base, such
17 as aqueous ammonia. High quality polyaniline nanofibers with
18 dopants ranging from mineral acids to organic acids can be
19 made. The synthesis is readily scalable and can be carried out
20 at room temperature.

21
22 In step 6, the polymer solution of polymers is separated
23 from the organic solution. This may be accomplished by
24 siphoning off the top floating polymer solution, and then
25 disposing of the spent organic solution. In step 7, the polymer
26 solution is purified into polyaniline nanofibers. The
27 purification step 7 can be accomplished by conventional
28 filtration or dialysis methods to effectively extract the

1 polymer nanofibers from the polymer solution. For example, the
2 purification can be by dialysis of the colloidal suspension
3 using standard commercially available dialysis membranes.
4

5 The polymer nanofibers are preferably conducting polymer
6 nanofibers having predetermined sizes, reactions, and
7 sensitivities to predetermined chemical vapors. The nanofibers
8 have nearly uniform predetermined diameters dependent upon the
9 specific acid used in the catalysis solution. The acidic anion
10 has a predetermined size, which when bound to the nanofiber
11 polymer backbone, affect the overall diameter size of the
12 nanofiber, having typical sizes mostly between 20 and 150 nm
13 and less than 500 nm. For example, hydrochloric acid produces
14 polyaniline nanofibers with a 30 nm diameter distribution, CSA
15 acid produces polyaniline nanofibers with a 50 nm diameter
16 distribution, and perchloric acid produces polyaniline
17 nanofibers with a 120 nm diameter distribution, all with
18 lengths varying from 500 nm to 5 μm . In the general form, the
19 nanofibers have diameters that are less than 500 nm and lengths
20 less than 10 μm .
21

22 Gram scale beaker production to kilogram scale vat
23 production can be used to synthesize various quantities of
24 production polymer nanofibers. The nanofibers are typically
25 twisted together forming an interlocking network or mesh of
26 nanofibers. That is, the nanofibers tend to agglomerate into
27 interconnected nanofiber networks, rather than bundles. Doping
28 and dedoping does not affect the fibrillar morphology. As such,

1 the networks of nanofibers have improved sensitivities, are
2 durable for repeated use, and are well suited for thin film
3 deposition on sensor terminals. The nanofibers can then be thin
4 film deposited onto conducting terminals on an insulating
5 substrate to form a sensor.

6
7 Referring to Figures 1A, 1B, 2, and 3, and more
8 particularly to Figure 3, an acid chemical sensor can be made
9 using polyaniline nanofibers when a method of forming an acid
10 sensor having steps 8-13. In step 8, purified polyaniline
11 nanofibers are disposed in a basic water solution for forming
12 an undoped polyaniline nanofiber solution. Discovery is made
13 that polyaniline nanofibers are stable in water, and can be
14 rapidly dedoped in water using a basic solution. In step 9, the
15 dedoped nanofiber polyaniline fibers are purified into a mass
16 of dedoped nanofiber polyaniline. In step 10, the dedoped
17 nanofiber polyaniline is disposed into water for forming a
18 working solution.

19
20 In step 11, the conducting terminals are formed on a
21 sensor substrate. The sensor substrate can be made of an
22 insulating material such as glass or quartz. The sensor
23 terminals can be made of a conducting material such as
24 semiconductors and conductors including gold, silver, platinum,
25 polysilicon and doped photoresist. In step 12, the working
26 solution is disposed onto sensor conducting terminals for
27 coating the terminals with the nanofibers. This coating step
28 can be accomplished by conventional coating methods such as

1 spin coating, drop coating, spray coating, and photolithography
2 masked deposition coating. In step 13, the working solution is
3 dried for coating a film of dedoped polyaniline nanofibers onto
4 the sensor conducting terminals. The nanofibers will then react
5 to the presence of various chemicals and solutions, such as an
6 acid causing a change in conductivity that can be sensed at the
7 sensor terminals.

8
9 Referring to Figures 1A, 1B, 2, 3, 4A, and 4B, and more
10 particularly to Figures 4A and 4B, polyaniline nanofibers
11 exhibit conductivity changes when dedoped or doped polyaniline
12 nanofibers are exposed to an acid or when doped polyaniline
13 nanofibers are exposed to a base. In the exemplar case, when
14 camphorsulfonic acid is used in the catalysis solution, the
15 polyaniline nanofibers have camphorsulfonic acid molecules are
16 tightly incorporated within the polyaniline during the in-situ
17 polymerization of aniline. Dedoped polyaniline nanofibers can
18 be obtained by dialyzing the camphorsulfonic acid doped
19 polyaniline against 0.1 M ammonium hydroxide, which produces
20 the emeraldine base form of polyaniline. Once the
21 camphorsulfonic acid molecules are removed, thin-film sensors
22 made of dedoped fibers respond to repeated doping and dedoping.
23 The sensor performance of the nanofibers having a predetermined
24 size diameter distribution, can be measured using a dedoped
25 nanofiber emeraldine base thin film, such as a 2.5 μm thick thin
26 film as compared to a conventional dedoped thin film, such as a
27 1 μm thick thin film that can be deposited on an array of
28 interdigitated gold electrodes. The sensor is exposed to an

1 acidic dopant, such as hydrochloric acid, for acidic doping,
2 and, then exposed to a base, such as ammonia, for basic
3 dedoping. The sensor, for example, may consist of fifty pairs
4 of electrodes at $4970 \times 20 \times 0.18 \mu\text{m}$ on a glass substrate with
5 interdigitated gaps of $10 \mu\text{m}$. The polyaniline nanofiber sensors
6 then exhibit a fast, predetermined reaction time during both
7 doping for acid vapor detection and dedoping for basic vapor
8 detection. The conducting polyaniline nanofibers possess fast
9 predetermined doping and dedoping times that are suitable for
10 sensor applications.

11
12 The real time resistance changes of a dedoped film can be
13 monitored using an electrometer upon exposure to an acid, such
14 as 100 ppm of hydrochloric acid HCl, as shown in Figure 4A, and
15 of a fully HCl doped film exposed to a base, such as 100 ppm of
16 ammonia NH_3 , as shown in Figure 4B. The resistance changes of a
17 nanofiber emeraldine base thin film and conventional thin film
18 upon exposure to 100 ppm HCl vapor and HCl doped films exposed
19 to 100 ppm NH_3 vapor are shown. The R/R_0 ratio is the resistance
20 R normalized to the initial resistance R_0 prior to gas exposure .
21 The nanofiber thin film responds faster than a conventional
22 film to both acid doping and base dedoping even though the
23 nanofiber film is more than twice as thick. This is due to the
24 small, predetermined diameter size of the nanofibers that
25 provides a high surface area within the film that can be
26 rapidly accessed by the gas vapors. Also, the small,
27 predetermined diameters of the fibers allow gas molecules to
28 diffuse in and out of the fibers in a much shorter

1 predetermined amount of time. This also leads to a much greater
2 extent of doping or dedoping over short times for the nanofiber
3 films.

4
5 Films of doped nanofiber and conventional polyaniline can
6 be measured and compared in response to exposure to alcohol
7 vapors, such as methanol, ethanol, and propanol, or to water
8 vapor. The mechanism of response in the case alcohol or water
9 exposure is not doping or dedoping but rather conformational
10 changes of the polymer film. The conformational changes produce
11 a resulting change in conductivity for use as an alcohol or
12 water vapor sensor. Again, the nanofiber sensor has a greater
13 response with a faster response time. In the case of volatile
14 organic chemicals, the response mechanism is swelling of the
15 polymer both in bulk film and in nanofiber forms. The swelling
16 also causes a resulting change in electrical conductivity,
17 which can be used to sense the organic vapor. Reducing agents
18 such as hydrazine react with polyaniline nanofibers to cause a
19 change in oxidation state and a corresponding change in
20 electrical conductivity and can be used to sense hydrazine.
21 The nanofibers can also react with chemical vapors with a
22 change in optical absorption qualities that can be detected
23 using coated optical detectors in the chemical sensors. In all
24 cases, the nanofiber films have improved sensor performance in
25 both sensitivity magnitude and time response as compared to
26 conventional bulk films for a range of analytes.

1 Referring to Figure 5, an enhanced sensor can be made by
2 precoating the gold terminal of a sensor with polyaniline prior
3 to a thin film in a method described in steps 14 through 24.
4 In step 14, conducting gold terminals are disposed on a sensor
5 substrate. In step 15, the gold terminals are exposed to 4-
6 Amino Thiophenol (4-ATP) for forming a thiol RSH surface layer
7 on the gold terminals. In step 16, the catalysis solution is
8 formed of water, acid, and oxidizer. In step 17, the monomer
9 solution is formed of the monomer and an organic solvent. In
10 step 18, the monomer solution is disposed in a reaction vessel.
11 In step 19, the sensor substrate is submerged in the vessel
12 with the gold terminals positioned at the surface of the
13 monomer solution. In step 20, catalysis solution is disposed
14 onto the monomer solution forming an aqueous organic reaction
15 interface flush with the gold terminals. A precoating of
16 polyaniline nanofibers is formed over upon the thiol RSH
17 surface layer while polyaniline nanofibers are also formed at
18 the interface and dispersed into the catalysis solution. In
19 step 21, the polymerization reaction is continued at the
20 aqueous organic reaction interface creating conductive, doped
21 polyaniline nanofibers that precoat the gold terminals while
22 creating conductive, doped nanofiber polyaniline in the
23 catalysis solution then becoming a polymer solution as the
24 monomer solution becomes an organic solution. Alternatively,
25 the polymerization reaction can also be continued to create a
26 polyaniline nanofiber film that results in a conducting
27 nanofiber film that spans electrodes to provide a complete
28 chemical sensor after washing of the resulting film. In step

1 22, the polymer solution is separated from the organic
2 solution, while the precoated substrate is removed from the
3 vessel. In step 23, the polymer solution is purified into
4 polyaniline nanofibers. In step 24, a film of the polyaniline
5 nanofibers is disposed over the precoated gold terminals for
6 forming a precoated sensor as shown in Figure 6.

7
8 Referring to Figure 6, a polyaniline nanofiber precoated
9 acid sensor includes the insulating substrate, at least two
10 gold terminals, including a positive gold terminal and a
11 negative gold terminal, upon both of which is disposed a thiol
12 (RSH) film and a polyaniline precoat. Over the precoated gold
13 terminals is disposed the thin film of polyaniline nanofibers.
14 The precoating offers enhanced adherence and contact
15 conductivity between the gold terminals and the polyaniline
16 film. When the polyaniline film is exposed to a chemical vapor,
17 the conductivity of the polyaniline film changes producing
18 changes in resistivity that would then produce a change in
19 electrical current as measured by a current meter that is
20 connected in series with a DC power source that is in turn
21 connected across the positive and negative gold terminals.

22
23 Referring to all of the figures, the synthesis method is
24 based on the chemical oxidative polymerization of a monomer,
25 such as aniline, in a strongly acidic catalysis solution having
26 an acid component, such as camphorsulfonic acid, and an
27 oxidant, such as ammonium peroxydisulfate. The polymerization
28 is performed in an immiscible organic-aqueous biphasic system,

1 in order to separate the by-products, including inorganic
2 salts, and oligomers, according to solubility in the organic
3 and aqueous phases. In an exemplar synthetic process, aniline
4 is dissolved in an organic solvent, such as CCl_4 , benzene,
5 toluene, or CS_2 while ammonium peroxydisulfate is dissolved in
6 water with camphorsulfonic acid. The two solutions are
7 transferred into a reaction polymerization vessel for
8 generating an interface between the two solutions. After a
9 short period, such as a few minutes, green polyaniline forms at
10 the interface and then gradually diffuses and disperses into
11 the aqueous phase of the catalysis solution. After an extended
12 period, such as several hours, the entire water phase is
13 homogeneously filled with dark green polyaniline, while the
14 lower organic layer appears red-orange, due to the formation of
15 aniline oligomers. The aqueous phase is then collected and the
16 by-products are removed by dialysis against deionized water,
17 using for example, tubing with a 12K to 14K cutoff. When a
18 deionized water bath reaches a pH of 7, a 10- μl suspension is
19 diluted with 1 ml of deionized water. Dedoped polyaniline can
20 then be obtained by dialysis using 0.1 M ammonium hydroxide and
21 then deionized water. The synthetic method produces yields
22 ranging from six to ten weight percent of nanofibers. Thin film
23 sensors made of the polyaniline nanofibers have superior
24 performance in both sensitivity and time response to a variety
25 of gas vapors including acids such as hydrochloric,
26 hydrofluoric, sulfuric, and nitric, bases such as ammonia and
27 butylamine, and alcohols such as methanol, ethanol, and
28 propanol. Thin film sensors made of the polyaniline nanofibers

1 are also sensitive to some volatile organics such as chloroform
2 and nitromethane, and to redox agents such as hydrazine.

3
4 The aqueous and organic interfacial synthesis of
5 polyaniline nanofibers has several advantages. Both the
6 synthesis and purification steps are template free. Uniform
7 nanofibers are obtained in high yields. The synthesis method is
8 scalable and reproducible with predetermined reactions and
9 response times. Multiple syntheses performed from millimolar to
10 molar quantities produce nanofibers of the same morphology,
11 size distribution and uniformity. The nanofibers are readily
12 dispersed in water, which facilitates environmentally friendly
13 processing and biological applications. The nanofiber sensors
14 have shorter doping and dedoping times with greater response to
15 acidic and basic gases. The nanofiber sensors have a faster and
16 larger response to alcohol vapors and react to some volatile
17 organics and redox agents. Chemical sensors made from the
18 nanofibers respond with larger magnitudes and faster response
19 times to a wide range of analytes, and are well suited for
20 chemical sensor applications.

21
22 The present invention is generally directed to a synthesis
23 method for forming polymer nanofibers. When the polymer
24 nanofibers are conductive, the resulting thin film can be used
25 in a chemical sensor. Conducting polymer nanofibers include
26 polyaniline nanofibers, polypyrrole nanofibers, and
27 polythiophene nanofibers all of which can be used in chemical
28 sensors. The method relies on the use of a monomer solution

1 comprising an organic monomer and an organic solvent, and the
2 use of a catalysis solution comprising an acid and an oxidizer,
3 for producing at an aqueous and organic interface
4 polymer nanofibers that preferably react to vapor exposures for
5 suitable use in chemical sensors. Various monomers, solvents,
6 oxidizers, and acids can be used as alternatives,
7 modifications, and improvements to the preferred forms. Those
8 skilled in the art can make enhancements, improvements, and
9 modifications to the invention, and these enhancements,
10 improvements, and modifications may nonetheless fall within the
11 spirit and scope of the following claims.

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